



# Post-Blast Analysis of Hexamethylene Triperoxide Diamine using Liquid Chromatography-Atmospheric Pressure Chemical Ionization-Mass Spectrometry



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## ABSTRACT

A qualitative method using liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (LC/APCI-MS) has been developed and validated for the identification of trace hexamethylene triperoxide diamine (HMTD) using three structurally-specific ions. Residues are extracted with deionized water (DI) and identified using a gradient mobile phase program and positive ion full scan mode on a Thermo Finnigan LCQ Ion Trap Mass Spectrometer. This method was validated according to several performance characteristics for the qualitative identification of an analyte using the characteristic ions, demonstrating the method's reliability for use on forensic applications. The method's limit of detection (LOD) can identify HMTD in an extract from a cotton matrix to which 20 µg of HMTD has been applied (equivalent to 10 ppm in extract). Previous scientific publications using LC/MS have not demonstrated post-blast HMTD residue analyses and suffer from a lack of chromatographic retention, sufficient number of mass spectral ions with validation, or require more complex/expensive instrumental methods (accurate mass or MS/MS). Post-blast analyses were successfully conducted with two syringe detonations that verified the efficacy of the method on the analysis of debris and residues following detonation.

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## 1. Introduction

The ability to detect and identify peroxide explosives has become particularly important in recent years due to their increasing prevalence in criminal and terrorist improvised explosive devices (IEDs) [1]. Peroxide explosives are organic compounds composed of one or more peroxide functional groups (R-O-O-R) and are separated into two classes: alkyl/acyl peroxides and cyclic peroxides [2,3]. Cyclic peroxides are

generally composed of 5-, 6-, or 9-membered rings, and fewer cyclic peroxide properties are known compared to the alkyl/acyl compounds [2]. Despite the lack of nitro- (NO<sub>2</sub>) groups in peroxide explosives, the O-O bonds may provide sufficient oxygen for rapid self-oxidation and explosion [1]. It is known that the cyclic peroxides detonate relatively easily, being sensitive to heat, friction, shock, and impact [1–4]. Therefore, cyclic peroxides are classified as primary explosives [1–3].

Two of the most commonly encountered cyclic peroxide explosives are triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD). HMTD is a white crystalline solid that was first synthesized in 1885 by L. Legler, and the accepted molecular structure is shown in Fig. 1 [2,5–7]. Its synthesis is relatively straightforward and requires three main components: hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), an acidic catalyst (including citric acid and other weak acids), and hexamine [4, 5]. Because these ingredients can be obtained as common household items from local stores, HMTD synthesis can be attempted by inexperienced chemists using basic laboratory equipment and chemical procedures found on the Internet. However, handling/producing it is dangerous due to its sensitivity to initiation. HMTD contains three peroxide linkages per molecule and generates 60% of the blast strength of TNT [1]. Its destructive power and explosive intensity combined with

*Abbreviations:* DI, deionized; FDA, Food and Drug Administration; GC/MS, gas chromatograph/mass spectrometer; HMTD, hexamethylene triperoxide diamine; HPLC/MS, high performance liquid chromatograph/mass spectrometer; IED, improvised explosive device; LC/APCI-MS, liquid chromatograph/atmospheric pressure chemical ionization-mass spectrometer; LC/MS, liquid chromatograph/mass spectrometer; LOD, limit of detection; MS/MS, mass spectrometer/mass spectrometer; NMR, nuclear magnetic resonance; RDX, cyclotrimethylene trinitramine; S/N, signal-to-noise; TATP, triacetone triperoxide; TIC, total ion chromatogram; TLC, thin layer chromatography; TNT, 2,4,6-trinitrotoluene.

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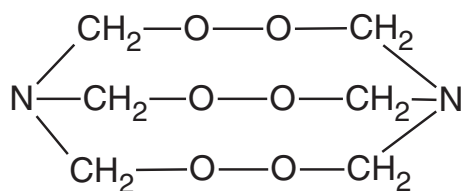


Fig. 1. Cyclic structure of HMTD (M.W. 208.17) containing three peroxide groups, first proposed by Baeyer and Villiger in 1900.

its general ease of production makes HMTD an attractive candidate for use in detonators in terrorist explosive devices when safer materials are not available [8].

According to media reports, peroxide based explosives were used in the July 7, 2005 London Underground bombings, and HMTD was carried by the al-Qaeda Millennium Bomber, Ahmed Ressam, for the planned attack on the Los Angeles International Airport in 1999 [1,8,9]. Also, two peroxide based explosive IED detonation attempts occurred on transatlantic flights, including American Airlines flight 63 in 2001 and a UK transatlantic flight in 2006 [1,8]. This series of high-profile terrorist plots involving peroxide-based explosives in the last decade made it crucial to be able to reliably identify these materials. However, it can be difficult to develop such methods because of the necessary sensitivity, low inherent spectroscopic response, and fragility of these compounds [7,8].

Current methods of testing for peroxide explosives include gas chromatography–mass spectrometry (GC/MS), high performance liquid chromatography–mass spectrometry (HPLC/MS), infrared spectrometry, nuclear magnetic resonance (NMR), thin layer chromatography (TLC), and HPLC-fluorescence [4,8]. The lack of chromophores or nitro- ( $\text{NO}_2$ ) groups, common to other explosives, makes the detection of peroxide explosives challenging because the common detection techniques in current use, including HPLC-Photo Diode Array Detection or nitrogen based detectors, cannot be employed [4,8,10]. Others have reported that LC/MS will successfully identify HMTD and TATP at trace levels, while GC/MS is a difficult technique due to the thermal decomposition it induces [2,4].

Previous research using LC/MS methods have successfully detected both HMTD and TATP simultaneously, but trace HMTD detection is compromised due to its overlap with the solvent peak using conditions which weakly retain it [4,11]. According to the Food and Drug Administration's (FDA) mass spectra acceptance criteria for identification using a single analysis method, three significant ions with relative abundances above 20% of the base peak should be monitored for molecular identification [4,12]. However, some have shown difficulty in generating HMTD spectra with a sufficient number of peaks to meet these criteria [4,13]. Also, although other LC/MS methods for HMTD detection have been published, most did not include a thorough method validation while monitoring at least three ions. The requirement of having three ions does limit sensitivity of a method when compared to previously published LC/MS studies using less stringent guidelines. Lastly, some have shown trace HMTD detection by LC/MS using direct injection of reference standards but have not demonstrated the method's success using actual post-blast samples [2,4,11,13,14].

In this study, a reliable technique for the identification of trace HMTD has been developed and validated using liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (LC/APCI-MS) and can be used for forensic applications. Extracts from swabs were tested to determine a method LOD instead of using direct injections of standards. This method monitors three molecular ions characteristic of HMTD while providing sufficient retention under a gradient method with minimal baseline noise. The mass spectrometer operates in full scan mode and eliminates the need for expensive accurate mass or MS/MS instruments. Most importantly, this technique demonstrates

a working method LOD and was successfully applied on actual post-blast debris without cleanup or concentration of the extracts.

## 2. Materials and Methods

### 2.1. Materials

Deionized (DI) water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ) was obtained using a Millipore Synergy Ultrapure Water System (Billerica, MA, USA). Acetone, citric acid, and ammonium nitrate were acquired from Fisher Scientific (Pittsburgh, PA, USA), while the reagent grade hexamine and hydrogen peroxide were purchased from Sigma-Aldrich (Pittsburgh, PA, USA). Caffeine, chosen as an internal standard, was obtained from Eastman Chemical Company (Washington, DC, USA).

The plastic explosive C-4 used to examine the method's selectivity was obtained from the Holston Army Ammunition Plant (Kingsport, TN, USA). HMTD was synthesized by experienced chemists at the FBI Laboratory and the material was verified using a known HMTD standard from AccuStandard, Inc. (New Haven, CT, USA). Synthesis of HMTD was necessary due to the large amount of explosive used for experiments and because solid material for purchase is not available. The stock solution used for all matrix fortification was prepared by dissolving 25 mg of freshly synthesized HMTD in 25 mL of acetone. The stock solution was diluted to the desired working concentrations with water to limit chromatographic peak broadening.

### 2.2. Instrumentation

The LC/APCI-MS system consisted of a Waters Alliance 2695 Separations Module connected to a Thermo LCQ DECA XP MAX mass spectrometer. The Alliance system contained the following components: pump, autosampler, injector, solvent mixing system, and membrane degasser. Chromatographic separation was achieved with an Alltech Alltima  $5 \mu\text{m}$  octadecyl (C18) analytical column (Fisher Scientific, Pittsburgh, PA, USA;  $2.1 \times 150 \text{ mm}$ ) at ambient temperature and a gradient mobile phase of water:methanol both containing 1.25 mM ammonium nitrate at a flow rate of 0.400 mL/min. Ammonium nitrate was added to the mobile phase to assist ionization by forming stable adduct ions. Peroxides are unstable under normal ionization conditions [14]. The injection size varied between 10  $\mu\text{L}$  and 50  $\mu\text{L}$ , and DI water served as the blank between injections. Table 1 contains the HPLC gradient program that is effective in HMTD separation.

HMTD identification was achieved with an atmospheric pressure chemical ionization source in positive mode (APCI+), heated capillary at 150  $^\circ\text{C}$ , source current 6.25  $\mu\text{A}$ , and a sheath gas flow setting at 56 psi. The vaporizing temperature was set to 360  $^\circ\text{C}$ , which is similar to what others found to provide a stable signal [4,11]. The MS operated in full scan mode with a mass range of  $m/z$  70.00 to 245.00. Caffeine was chosen as the method's internal standard because of the ability of APCI+ to efficiently ionize it under the method conditions and because the chromatographic method fully resolved HMTD and caffeine.

Xcalibur software was used for data processing. HMTD identification for all portions of the validation and the post-blast analysis was achieved if all three characteristic ions were present with signal-to-

Table 1  
HPLC gradient program for the single MS analysis of HMTD.

Time (Minutes)	Percent Methanol with 1.25 mM Ammonium Nitrate	Percent Water with 1.25 mM Ammonium Nitrate
0.00	10	90
2.00	10	90
12.00	50	50
14.00	50	50
17.00	10	90
20.00	10	90

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